

Chromium Stable Isotope Fractionation – An indicator of hexavalent chromium reduction.

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Introduction

Chromium is a common anthropogenic contaminant in surface water and ground water (Bartlett and James, 1988), and is also of interest in oceanography (Murray et al., 1983). It is redox-active; the two common valences in natural waters are Cr(VI) and Cr(III). Cr(VI) is highly soluble and toxic while Cr(III) is relatively insoluble and often co-precipitates with Fe-oxyhydroxides (Loyaux-Lawniczak et al., 2001). Redox conditions and reactions therefore control Cr mobility in aqueous solutions. Reduction of Cr(VI) to Cr(III) is the most important reaction controlling attenuation of Cr in solution and is presently the main focus of *in situ* remediation schemes (Blowes et al., 1997; Lytle et al., 1998).

Monitoring of Cr(VI) reduction *in situ* is therefore a critical goal and we propose that Cr stable isotopes ratios can be used to indicate reduction of Cr(VI). Mass dependent fractionation of Cr isotopes has not been systematically studied previously, but we expected from the outset that Cr(VI) reduction would favor the lighter isotopes and lead to enrichment of heavier isotopes in remaining Cr(VI) as is observed with sulfate, selenate, and nitrate reduction. We report here the first measurements of the magnitude of Cr isotope fractionation during Cr(VI) reduction.

Methods

Radiogenic variations of Cr isotopes have been used by meteoriticists for years, and thus TIMS methods are well established (Ball and Bassett, 2000). However, in order to measure mass-dependent fractionation, we had to develop a double-spike technique similar to that we use to determine Se stable isotope fractionation (Johnson et al., 1999). ⁵⁴Cr and ⁵⁰Cr are the spike isotopes used to monitor instrumental discrimination. We determine shifts in the ⁵³Cr/⁵²Cr ratios relative to the NBS 979 standard, and express the results as $\delta^{53}\text{Cr}$. Purification of Cr is done by ion exchange.

Experiments were conducted to measure abiotic Cr isotope fractionation during aqueous Cr(VI) reduction by 1) Fe²⁺ and 2) magnetite. Cr(VI) reduction by Fe²⁺ was complete in seconds or minutes, whereas the surface-catalyzed reduction with magnetite went to completion in three days. The instantaneous per mil fractionation, ϵ , was calculated assuming a Rayleigh fractionation model (Fig. 1).

Results

The ϵ for Cr(VI) reduction with Fe^{2+} was 1.0 ‰, whereas Cr(VI) reduction on magnetite surfaces yielded a greater fractionation of -3.6 ‰. The smaller fractionation occurring during reduction by Fe^{2+} is likely caused by the rapid rate of the reaction. We expect that the reaction rate was limited by the rate of diffusion of Cr(VI) into the plume of added Fe^{2+} , and thus the apparent fractionation should be less than that occurring during the reduction reaction. Reduction in the magnetite experiments was less rapid and thus the fractionations reflect isotope selection by the reduction reaction more directly.

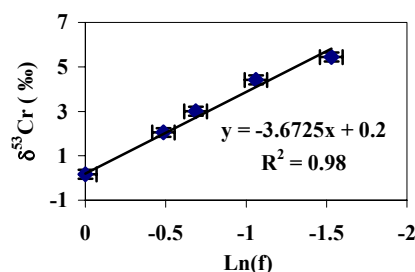


Figure 1. Cr(VI) reduction on magnetite surfaces. $\delta^{53/52}\text{Cr}$ of unreacted Cr(VI) vs Ln of unreacted Cr(VI) fraction. Slope = ϵ

Implications

The size of this Cr isotope fractionation is encouraging, as current precision is 0.1 to 0.2 ‰, depending on instrumentation. The next step is to examine fractionation by microbes and naturally occurring reductants other than magnetite. Presently we are performing sediment slurry experiments. If these reveal similar fractionations, Cr stable isotope analyses should be a highly practical indicator of the critical chromate reduction reaction, and an otherwise useful geologic and oceanographic tool.

References

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